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The Effect of Common Agrichemicals on the Environmental Stability of Polyethylene Films

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Abstract

The impact of commonly used agrichemicals (Paraquat, Mancozeb, Chlorpyrifos and Sulfur) on the environmental stability of polyethylene films has been evaluated under accelerated photo-oxidative conditions. Paraquat and Mancozeb when applied to unstabilized clear polyethylene film, followed by exposure to UV radiation, resulted in direct attack of the polymer, evident by faster rates of oxidation and shorter times to embrittlement compared to a polyethylene control. Reapplication of these chemicals during exposure, as often occurs in agricultural practice, resulted in even faster degradation. In contrast, Sulfur and Chlorpyrifos did not have a significant effect on the photodegradation of exposed unstabilized polyethylene film. When the polyethylene film was pigmented (white top layer containing rutile titanium dioxide and carbon black in the bottom layer) and stabilized with the addition of hindered amine stabilizers (HAS), differences in oxidation susceptibility were seen with repeated exposure to Paraquat showing the most dramatic effect. This was evident by an increased carbonyl index, decrease in elongation at break and an increase in tensile stress at yield compared to a control film and other agrichemical treatments. These studies enable degradation from accelerated consumption of stabilizers by the agrichemicals (and their degradation products) to be differentiated from enhanced photochemical initiation of the polyethylene degradation.

Keywords: polyethylene; mulch film; Paraquat; hindered amine stabilizer; agrichemical; degradation

1. Introduction

Polyethylene mulch films are commonly used in horticulture for a range of crops, including: tomatoes, capsicums and melons [1]. Mulch films must be cheap, easy to process and mechanically tough as they are used as a barrier to suppress weed growth and pest access [2].

The use of mulch films therefore allows lower levels of herbicides and pesticides to be employed. However, agrichemicals are still applied in combination with such films [3], and notably, several sulfur and chlorine-containing agrichemicals have been found to cause accelerated degradation of stabilized polyethylene [4-7]. It has been recognized that this is related to specific chemical reactions with the stabilizers that reduces their effectiveness and shortens service lifetimes.

Polyethylene mulch films are typically exposed to the outdoor environment for several months up to a year [8] before removal and disposal, and are required to retain their mechanical integrity on collection [1]. If the films have degraded during use in the field, fouling of the machinery used for collection can occur, and the fragments of plastic may disperse at random, providing an environmental hazard. Such wind-blown debris may also pollute rivers and lead to well-chronicled damage to aquatic systems [9]. To obviate this, hand collection may be required at significantly higher cost for the producer.

To prevent degradation caused by exposure to UV and heat, polyethylene mulch and crop propagation films have stabilizers added which either inhibit oxidation (hindered phenols) or retard it (hindered amines) [10]. Both stabilizer types act by interrupting the oxidation of polyolefins. The generally-accepted mechanism of oxidation involves the polymer peroxy radical $PO_2^{\bullet}$ as the chain carrier. The products from the reaction (1) of the peroxy radical $PO_2^{\bullet}$ with a reactive hydrogen in the polyolefin (PH) are the polymer hydroperoxide (POOH) and a new alkyl radical (P·).

$$PO_2^{\bullet} + PH \rightarrow POOH + P^{\bullet} \quad (1)$$

$$P^{\bullet} + O_2 \rightarrow PO_2^{\bullet} \quad (2)$$

The rapid reaction (2) of the alkyl radical with oxygen regenerates a peroxy radical so the oxidation reaction can continue. This process is still a linear chain reaction, however, and results in the accumulation of POOH as the oxidation product. Such hydroperoxides are stable in the dark at T<100^{o}C, but can decompose on exposure to UV or high temperatures to initiate further oxidation and ultimately result in polymer chain scission with the loss of mechanical properties. To combat this decomposition, hindered phenols are typically used as thermo-oxidative stabilizers. Such stabilisers act by deactivating $PO_2^{\bullet}$ radicals by converting them to POOH and by inhibiting the hydrogen abstraction reaction (1) and the subsequent production of more $PO_2^{\bullet}$. For UV stabilization, hindered amine stabilizers are preferred as they may directly decompose $PO_2^{\bullet}$ to inert by-products via a nitroxide intermediate in a catalytic process known as the Denisov cycle (Figure 1) [7].

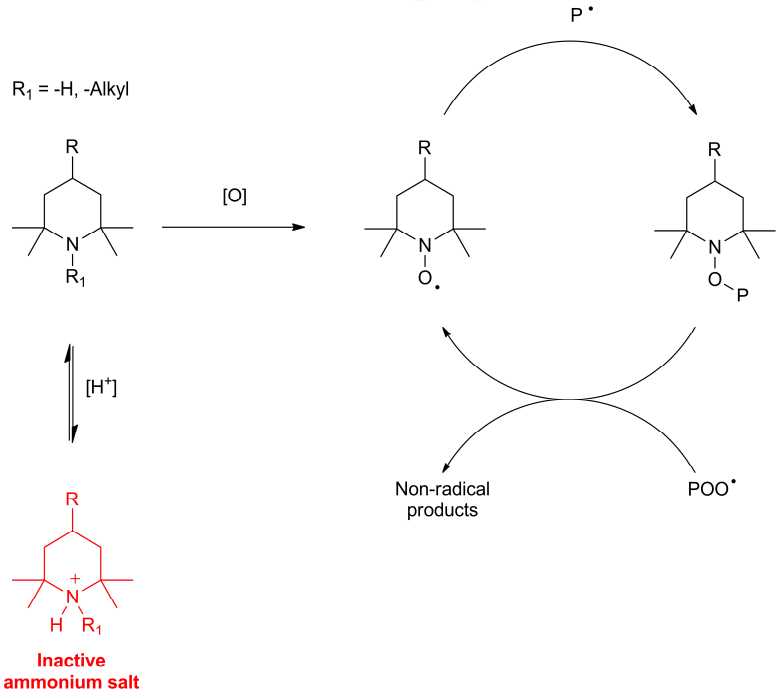

Figure 1. A simplified Denisov cycle showing that an acidified hindered amine is inactive and cannot take part in the radical scavenging cycle. Amine-type HAS are alkaline and can form inactive ammonium salts with acidic compounds as shown on the left. Adapted from [7, 11].

Hindered amine stabilizers (HAS) are commonly employed to protect agricultural film; however, there have been a number of reports on the negative effects of some agrichemicals on the efficacy of these stabilizers [4-7]. In polyolefin greenhouse applications, sulfur and chlorine-containing agrichemicals have been implicated in the suppression of activity of amine-type HAS due to chemical reactions of the acidic sulfur and chlorine-based compounds with the basic amine-type HAS. The ammonium salts produced in these reactions do not participate in the Denisov HAS stabilization cycle due to their inability to form the required nitroxide intermediate (Figure 1). Instead, they remain as inactive compounds and reduce the overall effectiveness of the stabilizer in the film.

In contrast to the effects of agrichemicals on stabilizers used in polyethylene mulch film, the effects of agrichemicals on the degradation of polyethylene, itself, are largely unknown. The resistance of polyolefins to direct chemical attack and their environmental persistence suggest they should be inert, which is distinctly different from agrichemicals. Agrichemicals are required to degrade rapidly in the environment and are subject to a range of abiotic degradation processes, such as UV degradation, which affects their environmental impact [12]. During these degradation processes, intermediate species capable of initiating degradation in polyethylene may be formed. In particular, the photochemical activation of the commonly-used herbicide and well known viologen, Paraquat (N,N'-dimethyl-4,4'-bipyridinium dichloride), generates free radicals such as superoxide [13-15], highly reactive species which may initiate degradation in polyethylene by consuming stabilizers and also potentially attacking the polymer. In addition, other agrichemicals, such as those based on dithiocarbamates which include the fungicide, Mancozeb, may potentially act as photo-prodegradants for polyethylene in the same way as deliberately engineered commercial degradable polyethylene film produced using a dithiocarbamate prodegradant technology developed by Scott and Gilead [8]. Therefore, the potential for agrichemicals to affect the

degradation of polyethylene, beyond stabilizer inactivation and through direct initiation, is significant.

To study the effects of agrichemicals on the degradation of polyethylene films, a range of common agrichemical types was chosen: Paraquat (a herbicide), Sulfur and Mancozeb (fungicides) and Chlorpyrifos (an insecticide) (Figure 2).

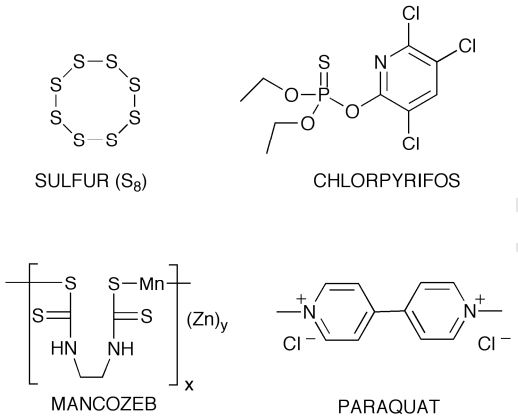

Figure 2. Chemical structures of the agrichemicals used in this study.

Both stabilized and unstabilized polyethylene films were studied in combination with individually-applied agrichemicals. The effects of these agrichemicals on the extent of oxidation of different types of polyethylene films under accelerated UV exposure are reported with the aim of differentiating effects due to stabilizer and intrinsic effects on the polymer.

2. Materials and Methods

2.1 Materials

A resin blend was used to form a base polyethylene matrix which is suitable for agricultural applications as a clear thin film. This mixture comprised two different LLDPE resins (Dow Plastics, major co-monomer: 1-octene), a low amount of LDPE (Qenos) and PIB as a tackifier (Daelim Corporation, M_w 2000 g/mol).

A commercially-available white-on-black LLDPE-based polyethylene mulch film, containing an amine-type HAS stabilizer was also evaluated. The white layer of the film contained a rutile titanium dioxide pigment and this side was exposed to the agrichemical and UV. The white layer of the white-on-black mulch film contained a total of 2.1 x 10^{-5} moles of active hindered amine functional groups/g of film. The film thickness was 27±1 microns.

Four different types of commercially available and commonly used agrichemicals were used: Mancozeb, 80% Sulfur, Paraquat, and Chlorpyrifos. The application rate of the active constituent within each agrichemical is summarised in Table 1. These agrichemicals were used at concentrations recommended by the agrichemical manufacturer's specifications for tomato farming.

Table 1. The application rates of the active constituent applied to the films for each agrichemical investigated.

Agrichemical	Active Constituent Application Rate (mol/ha)
Chlorpyrifos	2.8
Mancozeb	4.4
Paraquat	22.8
Sulfur	60.9

2.2 Clear Film Processing

Prior to blowing the clear film, the base resin masterbatch was passed through a 40 L/D twin, co-rotating Entek extruder with 27 mm diameter screws. The maximum temperature was 200°C and the screw speed was 50 rpm giving a residence time of between 3.75 and 4.0 minutes. A total of 300 g of processed material was then added to a 25 L/D Axon BX25 extruder fitted with a blowing die (215°C; 40 mm in diameter) and associated tower. The

blow-up ratio was a maximum of 3. The thickness of the final film was 14 ± 2 microns. The resins used to prepare the film contained minimal processing stabilizer only, added by the manufacturer. Extra stabilizer was not added during processing. The resulting film showed an oxidation induction time of 0 min at 190°C in oxygen atmosphere during differential scanning calorimetry-oxidation induction time (DSC-OIT) measurements, which indicates that the produced film contained little-to-no active phenolic processing stabilizer.

2.3 Agrichemical Treatment

The agrichemicals were applied onto the white layers of the white-on-black mulch films (the layer typically exposed to agrichemical and sunlight) or the clear films in a fume-hood, dried at room temperature (~22°C) and then aged. A series of experiments involving reapplication of agrichemicals were performed wherein the agrichemicals were reapplied every 6 days during aging. At the end of each aging cycle, samples were removed, measured for oxidation with FTIR-ATR (as described in Section 2.5) and tested for embrittlement by manually applying a small stress normal to the film plane. Embrittlement was noted when the films fractured multidirectionally under the applied stress.

2.4 Accelerated Photo-Oxidative Aging

The model system (clear unstabilized polyethylene film) and the white layer of the white-on-black mulch film samples after agrichemical treatment were exposed in a QUV accelerated weathering tester (Q-Lab, Ohio) under constant UV-A with an irradiance of 0.68 W/m^2 at 340 nm and a black panel temperature of 50°C.

2.5 Fourier Transform Infrared–Attenuated Total Reflectance Spectroscopy (FTIR-ATR)

At each measurement period (every 48 hours in most cases), a small area of film was cleaned with isopropanol and a lint-free tissue prior to measurement of the FTIR-ATR spectrum. A different area of film was cleaned and analysed each time to ensure the FTIR-ATR measurement was indicative of film exposed to an accumulated dose of agrichemical and UV. FTIR-ATR spectra were measured using a Nicolet 5700 FTIR spectrometer equipped with a Smart Endurance single bounce diamond-window ATR accessory using 32 scans and 4 cm^{-1} resolution over the range 4000-650cm^{-1} with a gain of 8 and a mirror velocity of 0.6329 cm/s. After initial acquisition using OMNIC software (Thermo-Nicolet, Madison, WI), spectra were manipulated and plotted using GRAMS/32 software package (Galactic Corp., Salem, NH). Oxidation was monitored using the carbonyl index (CI), which was measured as the height of the carbonyl stretching peak at 1714 cm^{-1} divided by the C-H bend peak height at 1463 cm^{-1}.

2.6 Tensile Testing

Analysis was performed on an Instron 5542 universal testing machine fitted with a 50 N load cell and pneumatic grips. Samples were 22 mm-wide with a grip separation of 25 mm and the long axis typically transverse to the machine direction. A crosshead speed of 250 mm/min was chosen based on an ASTM D882 standard test method. Reported values are quoted as the average ± 1 standard deviation of 6-8 replicate samples.

3. Results and Discussion

3.1 Effects of UV exposure

White-on-black mulch film is commonly used in subtropical and tropical environments during warmer seasons when UV levels are high. It is therefore susceptible to not only the possibility of extensive UV degradation, but also higher treatments of agrichemicals as a result of enhanced weed and pest growth during its seasonal application. To separate the effects of agrichemical application and UV exposure on the direct degradation of polyethylene compared to deactivation of stabilizers, both unstabilized clear polyethylene film and stabilized white-on-black mulch films were investigated in this study.

3.1.1 Model System: Unstabilized Clear Polyethylene Film

Paraquat, Mancozeb, Sulfur and Chlorpyrifos (Figure 2) were individually applied onto separate, unstabilized clear polyethylene films and exposed to UV-A radiation in a QUV accelerated weathering tester that simulates terrestrial exposure. The total UV exposure time that these films took to embrittle is summarised in Table 2. In all cases, each agrichemical was reapplied every 6 days, which reflects typical field re-application rates in times of rain.

Table 2. A summary of the number of days to embrittlement for unstabilized, clear polyethylene films treated with individual agrichemicals reapplied every 6 days and exposed in the QUV.

Film	Treatment	Days to Embrittlement*
Polyethylene	None (Control)	22±5
Polyethylene	Paraquat	13±1
Polyethylene	Mancozeb	17±1
Polyethylene	Sulfur	29±1
Polyethylene	Chlorpyrifos	23±1

*n=2, ±1 S.D.

The data in Table 2 and the carbonyl index data shown in Figure 3 demonstrate that Paraquat treated film was the fastest to oxidize and embrittle, followed by Mancozeb. The other treatments were not statistically different from the control film in oxidation rate (Figure 3) although the embrittlement time data suggest that Sulfur may have slightly stabilized the polyethylene film compared to the untreated control. However, the carbonyl index data suggest a slightly higher degree of oxidation for the Sulfur treated film compared to the untreated control film at longer aging times. That is, the film oxidizes slightly faster, but does not embrittle at the same level of oxidation.

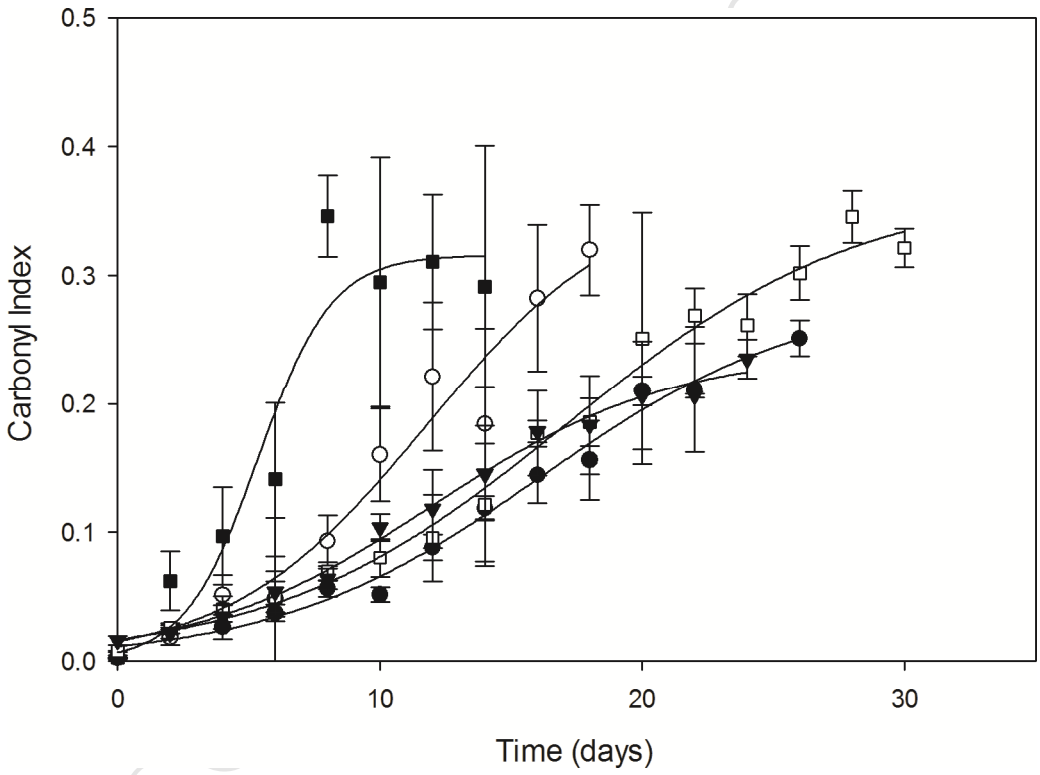

Figure 3. The evolution of carbonyl index until embrittlement for agrichemical-treated, unstabilized clear polyethylene film samples: Control (●), treated with Mancozeb (○), treated with Paraquat (■), treated with Sulfur (□) and treated with Chlorpyrifos (▼). All treatments were reapplied every 6 days.

The carbonyl index and embrittlement data for Chlorpyrifos and Sulfur treatments indicate that these agrichemicals do not have a significant effect on the oxidative photodegradation of unstabilized polyethylene film. In contrast, the faster rates of oxidation and shorter

embrittlement times for Paraquat and Mancozeb-treated films are consistent with both of these agrichemicals being photo-prodegradants for polyethylene, itself.

The photoactivity of dithiocarbamate transition metal complexes such as Mancozeb is dependent on the metal ion in the complex, where iron and manganese complexes are sensitizers [16] and zinc and nickel complexes have a stabilizing effect [17]. Mancozeb's chemical structure includes a zinc ion coordination product with a manganese ethylenebisdithiocarbamate polymer [18]; therefore, the photo-oxidation rate may be controlled by the relative amounts of Zn(II) complex (2% Zn^{2+}: stabilizer) and Mn(II) ethylenebisdithiocarbamate (16% Mn^{2+}: photosensitizer) [19] as shown for other mixed metal dithiocarbamate systems [20]. During UV exposure, Mn(II) ethylenebisdithiocarbamate can cleave to form dithiocarbamoyl radicals that may directly attack polyolefins [21]. Further reactions include oxidation to the corresponding sulfides with the liberation of the metal [20] and formation of further oxidation products such as sulfur-containing acids [22]. The liberated transition metals can enhance the decomposition rate of hydroperoxides and accelerate disintegration of the polymer [20]. A summary of these processes is shown in Figure 4.

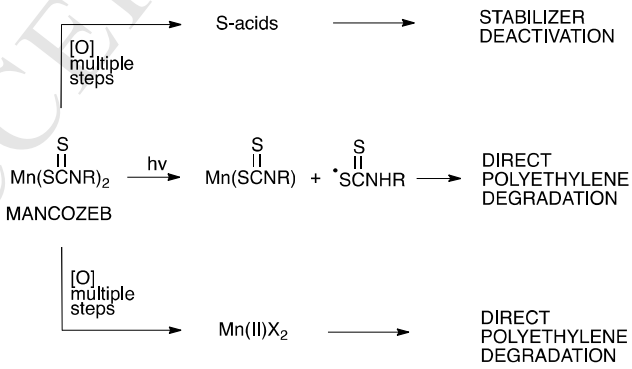

Figure 4. UV degradation pathways for Mancozeb that potentially lead to direct polyethylene degradation or amine-type HAS stabilizer deactivation [20-22].

The mechanism of action of Paraquat as a herbicide involves the production of superoxide; a known degradant for polyethylene [23]. The formation of superoxide in the presence of Paraquat occurs by a two-stage, catalytic process where the Paraquat first undergoes one-electron reduction to give the radical cation (Paraquat$^{\bullet+}$), followed by reaction with oxygen to give superoxide and regenerate Paraquat (PQ^{2+}) [24] (Figure 5). In plants, the one-electron reduction process to give Paraquat$^{\bullet+}$ is facilitated by the photosynthetic system [25], and can be simulated *in vitro* by a range of photoreductants as summarised in Ebbesen *et al.* [26]. However, there are no photoreductants inherently present on polyethylene, so another pathway to produce Paraquat$^{\bullet+}$ must occur if Paraquat is to act as a photo-prodegradant on UV-exposed polyethylene, as shown by the data in Figure 3. Direct photoreduction of Paraquat can occur in the presence of alcohols, alkaline and acid solutions, neutral aqueous solution [26] and when absorbed on solid cellulose [27]. It is therefore likely that direct photoreduction can also occur from oxidation product impurities (e.g., carbonyl and hydroxyl groups) present in the polyethylene as a consequence of synthesis or processing.

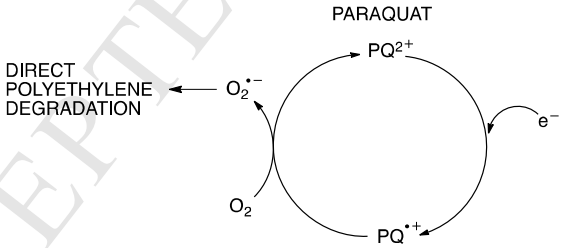

Figure 5. UV degradation pathway for Paraquat that potentially leads to direct polyethylene degradation [24].

In addition to the direct photo-prodegradant effect of Paraquat, there may also be another prodegradant effect due to its quaternary ammonium salt structure. Quaternary ammonium salts have been proposed to form adducts with hydroperoxides and accelerate their decomposition, with the activity of the salt being dependent on the structure of the cation and

the type of counter-ion present [28-30]. In the presence of ammonium halide compounds, which may include Paraquat (Figure 2), decomposition of hydroperoxides to form alkoxy and halide radicals has been proposed [29, 30]. These radicals may act as initiators in the autoxidation of hydrocarbons such as polyethylene. However, bulky cations may affect the formation of these radical species. It has been found [30] that the autoxidation of ethylbenzene was initially inhibited in the presence of quarternary ammonium salts with bulky cations due to decomposition of ethylbenzene hydroperoxides to by-products such as acetophenone and 1-phenylethanol.

Overall, the data for UV-treated, unstabilized polyethylene films indicate that some agrichemicals can have a significant accelerating effect on oxidative degradation rates. The effect that these photo-prodegradant agrichemicals have on unstabilized film degradation has, to the best of our knowledge, not been previously evaluated. With the knowledge gained from the study of unstabilized film, further tests were performed on commercially-produced, HAS-stabilized white-on-black polyethylene mulch films as a means to understand how agrichemical application may affect the degradation of film used in the field.

3.1.2 Stabilized Pigmented White-on-Black Mulch Film

The effect that the four different agrichemicals had on the UV-induced degradation of the commercial white-on-black mulch film was investigated to evaluate the impact of the agrichemicals on both the polymer and the stabilizer used within the films. The effect of reapplying the agrichemicals was studied by comparing the aging of films that had a single application of agrichemical (followed by UV exposure), with samples that had the agrichemicals reapplied every 6 days during UV exposure.

Figure 6 shows the carbonyl index (CI) *versus* QUV exposure time for the white-on-black mulch film exposed to the four different agrichemicals, with the final carbonyl index values

(70 days UV aging) shown in Figure 7. None of the films reached embrittlement after the 70 day ageing period but there were changes in mechanical properties and differences in the rates of oxidation.

Of significance for farming practice where multiple applications are undertaken is the impact that reapplication of agrichemicals has on the film oxidation rate. The observed oxidation rates for samples that had reapplied agrichemical treatments were typically higher than oxidation rates observed for samples that had single applications of the agrichemicals. The rate of oxidation as shown by the carbonyl index growth with UV aging for white-on-black mulch film treated with Paraquat was higher than other treatments, followed by Mancozeb-reapplied samples. This is consistent with these agrichemicals being photo-prodegradants as shown for unstabilized polyethylene film, above. In addition to the direct photo-prodegradant effect of Mancozeb, further oxidation products (sulfur-containing acids) from the sulfides produced during Mancozeb decomposition may also deactivate amine-type HAS stabilizers as shown in Figure 1, Figure 4 and Figure 8.

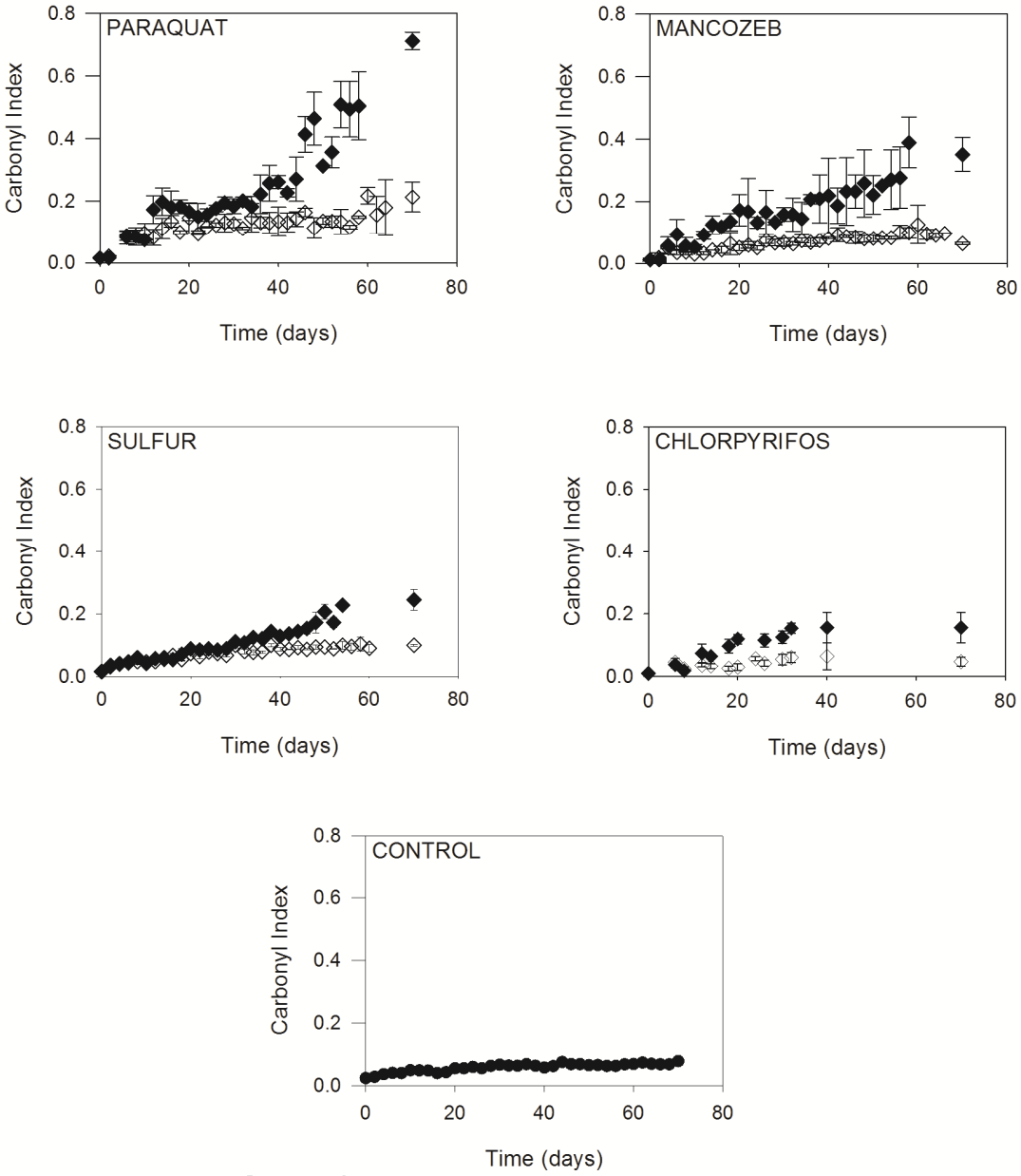

Figure 6. The change in carbonyl index with time for UV-treated white-on-black mulch films, both with and without agrichemical treatment. White-on-black film Control without agrichemical treatment (●), white-on-black film: one application of agrichemical (◊), white-on-black film: reapplied agrichemicals (♦).

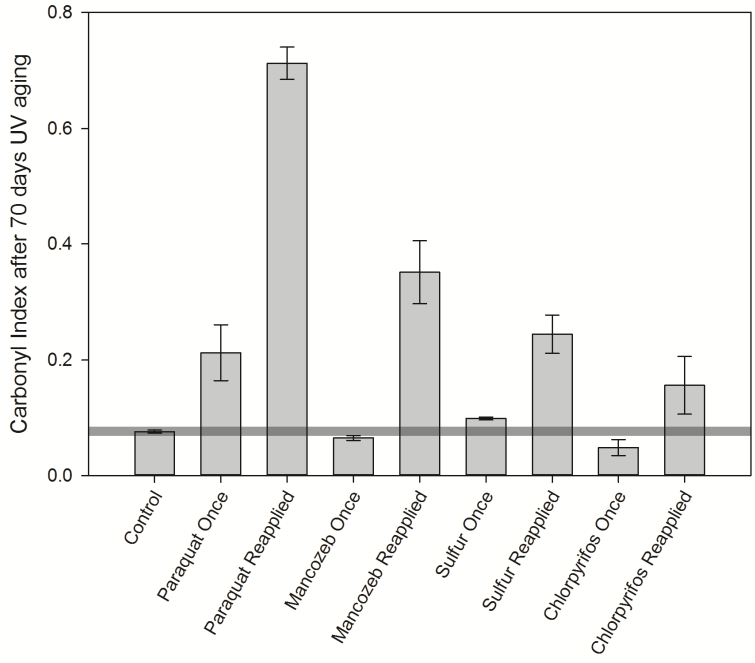

Figure 7. Carbonyl index values after 70 days of UV aging for agrichemical-treated white-on-black mulch films. The carbonyl index values for untreated, UV-aged Control samples have been extended across the figure using a semi-transparent bar to indicate which treatments showed enhanced oxidation rates.

In contrast to the unstabilized film study, Sulfur reapplication on the white-on-black mulch film showed enhanced oxidation compared to the untreated film. This is consistent with this sulfur-based agrichemical deactivating the amine-type HAS used as a stabilizer in this film, rather than it acting as a direct photo-prodegradant. Sulfur and chlorine-containing agrichemicals are known to deactivate amine-type-HAS stabilizers by acid formation and direct chemical reactions that reduce the active HAS concentration (Figure 1, Figure 8 and Figure 9) [7].

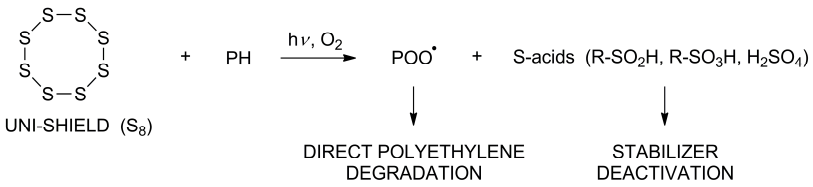

Figure 8. UV degradation pathways for Sulfur that potentially lead to direct polyethylene degradation or amine-type HAS stabilizer deactivation. Adapted from [7].

Chlorpyrifos treatment only slightly affected the rate of oxidation in the white-on-black film where reapplication was used. The effect was not as significant as that found for the other reapplied agrichemical treatments on this film type. This suggests that Chlorpyrifos is less effective as a degradant compared to the other agrichemicals studied. Since Chlorpyrifos-treated, unstabilized polyethylene films did not show enhanced oxidation compared to untreated control samples (Figure 3), it was concluded that it did not act as a direct photo-prodegradant for polyethylene. Instead, any prodegradant effect that it has on stabilized film must be due to attack on the HAS stabilizers. The first step in the photo-oxidation/photo-hydrolysis of Chlorpyrifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate) has been reported to produce products that include: a de-ethylated product (O-ethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothioate), the (photo)hydrolysis product (3,5,6-trichloro-2-pyridinol) and the oxidation product O,O-diethyl-O-(3,5,6-trichloro-2-pyridinil) phosphate (Figure 9) [31]. The photodegradation of Chlorpyrifos to form 3,5,6-trichloro-2-pyridinol is much slower than the subsequent photolysis of this degradation product. Photolysis of 3,5,6-trichloro-2-pyridinol occurs via the loss of chlorine [32], which may lead to deactivation of amine-type HAS stabilizers through the formation of HCl in a mechanism analogous to that reported in [7] and shown in Figure 9. The other (photo)hydrolysis product from Chlorpyrifos is di-ethyl thionophosphoric acid, which may act as a photostabilizer as shown for di-butyl thionophosphoric acid in polypropylene [33]. The photostabilizing effect of this degradation product may, in part, help to explain why the carbonyl index values at 70 days are lower than

the sample with no agrichemical treatment (see Figure 7); however, this was not seen for film reapplied with Chlorpyrifos where the production of both di-ethyl thionophosphoric acid and HCl would be higher. The effectiveness of Chlorpyrifos as a photo-prodegradant may also be affected by its high volatility. Notably, the half-life for volatilisation from an inert surface at 25°C has been reported to be 8 hours [32].

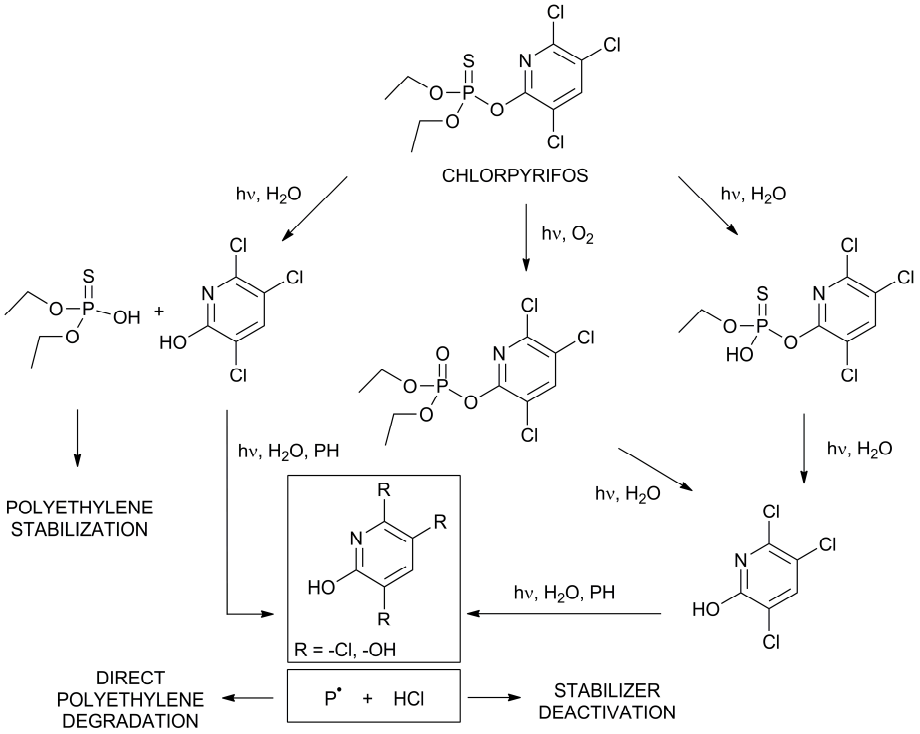

Figure 9. UV degradation pathways for Chlorpyrifos that potentially lead to direct polyethylene degradation, stabilization and amine-type HAS stabilizer deactivation [31-33].

3.1.2.1 Mechanical Properties of the Agrichemical-Treated White-on-Black Films

Since embrittlement was not observed after the 70 day ageing period for the white-on-black films, mechanical testing was performed on these samples to assess whether or not significant structural changes had occurred. Changes in elongation-at-break and tensile stress at yield were monitored since both of these factors are indicative of structural changes in polyethylene due to photodegradation [34]. Reapplication of Paraquat to white-on-black film showed the most dramatic reduction in elongation compared to the virgin material (Figure 10) and, to a much lesser extent, a reduction in elongation was also noted for Mancozeb- and Chlorpyrifos-treated films. Similar trends were observed in the tensile stress at yield data, where the Paraquat-treated film showed the highest tensile stress at yield, followed by Mancozeb and Chlorpyrifos treatment; all higher than the virgin material (Figure 12), suggesting crosslinking or a change in the crystallinity of the film had occurred during UV exposure after agrichemical treatment. The trends in the mechanical testing data were consistent with the trends observed in the carbonyl index data after 70 days aging, which indicates that Paraquat-treated film showed the highest degree of degradation after UV aging (Figure 7). Trends in the elongation-at-break and tensile stress at yield data were not as obvious for films tested in the machine direction (Figure 11 and Figure 13).

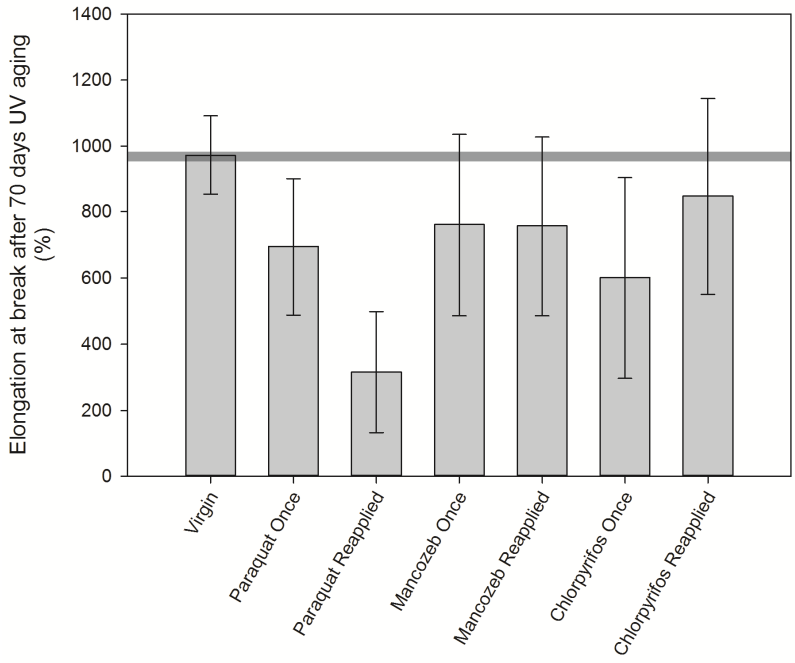

Figure 10. The elongation-at-break for Virgin, Paraquat, Mancozeb and Chlorpyrifos-treated (one application or reapplied) white-on-black film after 70 days UV exposure. The virgin film was not exposed to UV. All films were tested in the transverse direction. The mean for the Virgin sample has been extended across the figure using a semi-transparent bar to indicate which treatments showed changes in elongation-at-break.

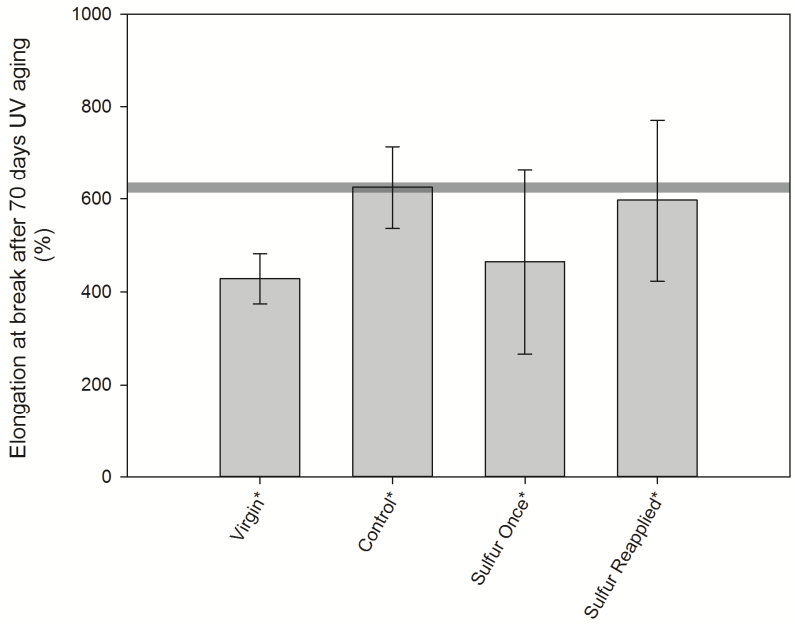

Figure 11. The elongation-at-break for Virgin, Control and Sulfur-treated (one application or reapplied) white-on-black film after 70 days UV exposure. *All films were tested in the machine direction. The mean for the UV-aged Control sample has been extended across the figure using a semi-transparent bar to indicate which treatments showed changes in elongation-at-break.

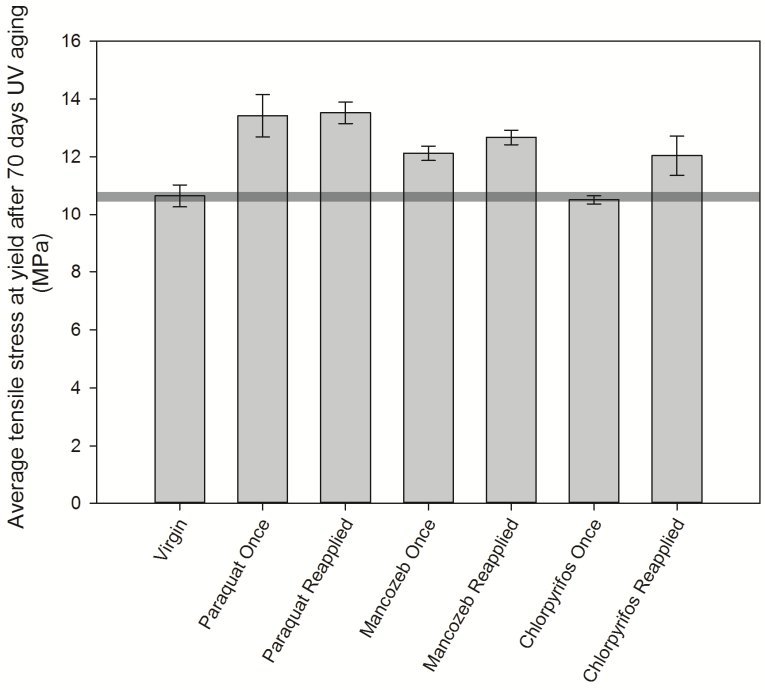

Figure 12. The tensile stress at yield for Virgin, Paraquat, Mancozeb and Chlorpyrifos-treated (one application or reapplied) white-on-black film after 70 days UV exposure. The Virgin film was not exposed to UV. All films were tested in the transverse direction. The mean for the Virgin sample has been extended across the figure using a semi-transparent bar to indicate which treatments showed changes in tensile stress at yield.

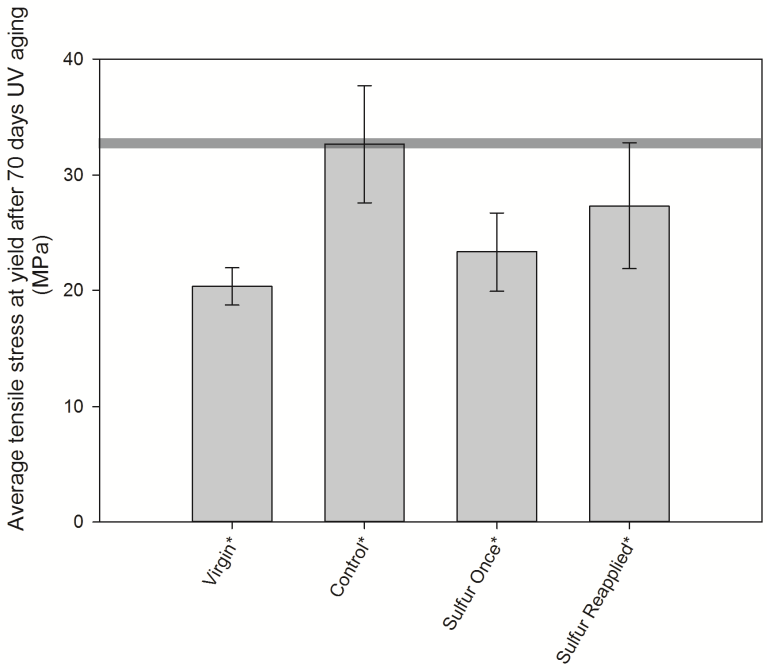

Figure 13. The tensile stress at yield for Virgin, Control and Sulfur-treated (one application or reapplied) white-on-black film after 70 days UV exposure. *All films were tested in the machine direction. The mean for the UV-aged Control sample has been extended across the figure using a semi-transparent bar to indicate which treatments showed changes in tensile stress at yield.

4. Conclusions

The effect of several commonly-used agrichemicals (Paraquat, Mancozeb, Sulfur and Chlorpyrifos) on the UV-induced degradation of polyethylene film was investigated. Of these, Paraquat was found to have the strongest impact on degradation for both film types, suggesting that it directly attacks polyethylene during UV irradiation.

For clear film without added stabilizer, both Paraquat and Mancozeb were found to accelerate the oxidation rate. In contrast, Sulfur and Chlorpyrifos had no significant effect on oxidation rates. These results indicate that Paraquat and Mancozeb can act as photo-prodegradants for polyethylene itself, in contrast to Sulfur and Chlorpyrifos which did not directly affect the UV degradation rate of polyethylene.

The commercially-prepared, HAS-stabilized white-on-black mulch films showed higher rates of oxidation for most of the agrichemical-treated samples compared to an untreated control white-on-black film. Increased degradation rates over the untreated control sample for Sulfur and Chlorpyrifos are consistent with HAS stabilizer consumption via the formation of acidic by-products as these agrichemicals did not show direct photo-prodegradant effects for clear film. As observed for clear film, it was found that the effect of repeated application of Paraquat was greater than any other agrichemical and this was attributed to direct attack on the polyethylene as well as stabilizer consumption. The mechanism for accelerated oxidation may be the production of superoxide from atmospheric oxygen by the Paraquat radical cation ($Paraquat^{\bullet+}$) that is formed following the one-electron photoreduction of Paraquat, or accelerated decomposition of hydroperoxides due to interaction with the Paraquat quaternary ammonium salt.

This study has shown that the effects of agrichemical use on mulch film degradation arise not only by attack on the HAS stabilizer used in the film, but also the inherent photochemistry of applied agrichemicals and the frequency of re-application. Therefore, it is important to take into account agrichemical type, along with weather conditions (UV, heat and rainfall) when applying agrichemicals to polyethylene mulch film so that premature film degradation and negative environmental impact can be avoided.

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